

# DEVELOPMENT AND EVALUATION OF DEEP-SEA SWIMSUIT MATERIALS



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NAVY CLOTHING AND TEXTILE RESEARCH UNIT

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DEVELOPMENT AND EVALUATION OF DEEP-SEA SWIMSUIT MATERIALS

by

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## ABSTRACT

The Navy Clothing and Textile Research Unit (NCTRU) has developed a swimsuit material that meets the requirements of Navy personnel who operate at great sea depths for long periods of time. Two chemically distinct, flexible, syntactic foams--a Unit-developed, polyurethane, hollow-glass-microsphere composite and a proprietary, polyvinylchloride, hollow-glass-microsphere composite--have been produced which may prove useful for swimsuit applications in deep-sea environments down to 1000 FSW.

Tests showed that both materials were essentially incompressible to depths of 1000 FSW (less than 3%) and provided more insulation than currently used Neoprene-foam materials at depths greater than 20 FSW. The materials, however, were considerably heavier than the foam although significantly less dense than sea water.

Standard wet-style swimsuits were fabricated from these experimental materials for verification of sample thermal-conductivity data. Suit conductivity tests performed on an instrumented copper manikin substantially confirmed the material test data obtained with a guarded hot-plate device. During construction of the suits it also became apparent that special designs and fabrication techniques would have to be developed to utilize these materials most effectively.

The thermal-conductivity results measured for both material composites were higher than expected based upon theoretical derivations, indicating that further improvements may be possible in this property. The higher conductivity values may indicate that, when the material is compounded, some of the spheres may be fractured. As a result, solid-glass particles coexist with the hollow spheres, limiting to some degree the ability of the spheres to reduce conductivity to the expected level.

Since the many efforts to approach optimum values have failed, it seems this goal is not easily achievable. It is therefore felt that further development would produce a material only nominally better than the polyurethane and PVC composites. It is recommended that future efforts be expended on the special suit design and fabrication problems that these materials require to best use their particular characteristics.

## DEVELOPMENT AND EVALUATION OF DEEP-SEA SWIMSUIT MATERIALS

### INTRODUCTION

*Paragraph replaced see serial 1 sheet on serial 1 cover J.W.*

The Navy Clothing and Textile Research Unit (NCTRU) has developed a swimsuit material that meets the requirements of Navy personnel who operate at great sea depths for long periods of time. NCTRU has tested this Neoprene foam and learned that it is inadequate for diving to great depths since it loses its insulative ability in deep water. NCTRU decided to develop this material because it was well-known in the diving community that the Neoprene foam now used in the diver's suit material could not fulfill all of the demands of deep-sea diving (1).

The Neoprene foam is a closed-cell material which provides insulation by the entrapment of nitrogen within the individual cells. Because of its structure, Neoprene, even when subjected to pressures equivalent to as little as 10 feet of salt water (FSW), compresses as much as 13% of its original thickness and will compress to 62% (50% of its original thickness in 100 FSW) of its original thickness in 1000 FSW. (A maximum sea-water depth of 1000 feet was used as a study limit since it would encompass man-underwater exploration and expected work situations for continental-shelf applications.) This reduction of material thickness significantly increases heat conductance, thereby making it almost impossible for a diver to remain warm for any length of time in deep water. In addition, the loss of material thickness under pressure seriously influences buoyancy and possibly flexibility. This loss in buoyancy with increasing pressure could impair the diver's control of his depth. Material compression may also cause the material to stiffen which would make it more difficult for a diver to maneuver and would impair his relative comfort.

These properties of Neoprene foam which make it unacceptable for deep-sea diving highlighted the need to acquire or develop a material commensurate with deep-sea-diver's suit requirements. In addition, it was necessary that any newly developed material should have the propitious properties that make Neoprene a desirable, shallow-water, swimsuit material.

The performance parameters considered important for a suitable, deep diver's, swimsuit material were as follows:

(a) Low Thermal Conductivity--lower than Neoprene foam (0.04 BTU/hr ft °F) if possible but allowably higher if the material were incompressible.

(b) Material "K" factor to be unaffected by depth pressures. (The insulative value of the material should be essentially the same at salt water depths of 1000 feet as it is at sea level.)

(c) Material shall be incompressible when subjected to three-dimensional hydrostatic heads of 1000 FSW so that insulative and buoyancy properties at sea level are not appreciably compromised.



(d) Material shall be drapeable and stretchable to the extent that it can be used to fabricate a swimsuit without creating undue discomfort to the swimmer when exercising his joints. The material should maintain drapeability at temperatures down to 0°F.

- (e) Water impermeability.
- (f) Low density.
- (g) Good abrasion resistance.
- (h) Good tear-strength properties.
- (i) Non-flammability.
- (j) Low outgassing characteristics.

In order for the developed material to be uniquely suited to deep-sea diving operations, consideration had to be given to saturation diving conditions and surface diving situations in which divers live in a habitat with a predominately helium atmosphere. Under such conditions, the compression effects on Neoprene mentioned above cause concern. It has been shown that: (a) with repetitive use at saturation diving conditions the nitrogen gas normally contained within the material cells is replaced with helium, reducing the inherent insulation (thermal conductivity of helium is 6 times greater than nitrogen--.083 vs .014 BTU/hr ft °F); and (b) the cyclic action of leaving the habitat, entering the water, and returning to the habitat causes some loss of the entrapped helium which results in a permanent loss in material thickness up to 40% (1).

The purposes of this report are to describe a NCTRU-developed, polyurethane composite material and to detail its performance characteristics and those of a proprietary, PVC material. The report also recommends further direction in the development and use of these materials.

#### PRELIMINARY DEVELOPMENT

##### Initial Materials

NCTRU contacts with industry and government agencies revealed that there were no commercially available materials, but several manufacturers had in-house developments underway for a deep-sea diver's suit material. A survey of these materials revealed that, in all cases, further development was necessary. Of the materials initially observed, further industrial development continued on only two candidates. Moreover, the manufacturer of only one of these two continued to send samples to NCTRU for appraisal and recommended improvements. NCTRU monitored only this material, because other Navy agencies had studied the remainder of the candidates.

All of the material samples initially received either used a syntactic foam approach or sandwiched rigid, non-compressible elements within an impermeable jacket. None of these materials were considered suitable in the form received. The best of these materials--two, syntactic foam-types--showed at least some potential. One was a polymerized-oil, hollow-glass-microsphere composite and other was polyvinylchloride, hollow-glass-microsphere composite (PVC). The former was being studied by other Naval agencies. This Unit has closely followed the PVC development.

#### Thermal-Conductivity Data

The initial PVC specimens showed acceptable thermal conductivity (.064 BTU/hr ft °F\*) and were essentially incompressible. The material appeared to be uncured, however, and continuously exuded an oily mixture. It eventually degraded. Subsequent industrial development produced a much improved, non-degradeable, vinyl composite. This latter material, however, showed a somewhat higher thermal conductivity value than the original one (.072 BTU/hr ft °F\*). Table I lists some of the thermal conductivity data obtained on some of the original sample materials received from industrial sources.

All of these materials were considered unsuitable for this deep-sea diving suit application because they were either: too rigid, not water impermeable, not properly cured, too heavy, or a combination of these reasons.

Some of the expressed microsphere concentrations given in Table I do not coincide with measured densities. Table II lists the calculated values based upon specific weights for Latex of 60.5#/ft<sup>3</sup>, Neoprene 76.5#/ft<sup>3</sup>, PVC 88#/ft<sup>3</sup>, Urethane 84#/ft<sup>3</sup>, and glass microspheres 16.6#/ft<sup>3</sup>. As can be seen there is substantial agreement in some cases and very poor agreement in others. Because of significant density differences between the glass particles and the resins, the particles tend to concentrate at the top of the liquid mix when the materials are formed unless some mechanical mixing is done. Thus, final concentrations may not be uniform throughout the material. Consequently, when the final specimen is trimmed, the particle concentration obtained may be more or less than that expected.

Figure 1 depicts measured thermal conductivity data for these specimens versus the calculated volume particle concentration. As particle concentration increases, conductivity seems to decrease. In reality, however, this relationship was not as strong as expected. Variations in calculated particle concentrations from those reported when samples were blended (Table II) indicate that, in the case of the Neoprene samples, some of the glass spheres may have fractured and become solid-glass elements in the matrix, thereby offsetting the reduction in conductivity expected by increasing particle concentration (Figure 1). The variation in the Latex-sample thermal conductivity for the same calculated concentration (Figure 1) could have been caused by the use of different Latex compositions in the samples leading to an erroneously calculated concentration, the degree of particle breakage, or dispersion differences. The one PVC and the Urethane specimen tested showed essentially the same conductivity value even though the particle concentration was considerably different. Their conductivities were essentially equal to the unfilled Neoprene specimen.

\* As measured by the Cenco Fitch Method.

Table I. Thermal Conductivity Data on Initial Candidate Swimsuit Material from Industrial Sources.

Material Description *	Density #/ft <sup>3</sup>	Thick (in)	Thermal Conductance BTU/hr ft <sup>2</sup> °F**	Thermal Conductivity BTU/hr ft °F**	Remarks
Neoprene Foam	16.9	0.250	1.82	.038	Current Wet Suit Material
Neoprene Jacket with Hard Rubber Wafers Inside	24.0	0.240	1.95	.039	Not Water Impermeable; Semi-Rigid
Neoprene Jacket with Hollow Glass Microspheres Inside	25.8	0.204	3.31	.056	Not Water Impermeable; Semi-Rigid
Syntactic Foam Materials Latex with 10% hollow Glass Microspheres by Wt.	40.3	0.168	4.06	.057	Semi-Rigid
Latex with 23% hollow Glass Microspheres by Wt.	40.7	0.096	5.74	.046	Semi-Rigid
PVC with 50% hollow Glass Microspheres by Wt.	34.6	0.216	3.90	.064	Degraded with time
Urethane with 40% hollow Glass Microspheres by Vol.	55.0	0.276	2.92	.067	Semi-Rigid
Solid Neoprene	76.5	0.252	3.20	.067	Heavy and not very flexible

Table I. Thermal Conductivity Data on Initial Candidate Swimsuit Material  
from Industrial Sources. (Cont'd)

Material Description *	Density #/ft <sup>3</sup>	Thick (in)	Thermal Conductance BTU/hr ft <sup>2</sup> of**	Thermal Conductivity BTU/hr ft of**	Remarks
Neoprene with 4.2% Hollow Glass Microsphere by weight	68.2	0.240	3.84	.077	Semi-Rigid
Neoprene with 8.5% Hollow Glass Microsphere by weight	63.6	0.252	3.31	.070	Semi-Rigid
Neoprene with 17.5% Hollow Glass Microsphere by weight	63.5	0.252	3.42	.072	Semi-Rigid
Neoprene with 27.6% Hollow Glass Microsphere by weight	62.5	0.252	3.58	.075	Semi-Rigid

\* Manufacturer's Descriptions

\*\* Cenco Fitch Method

Table II. Calculated Glass-Microsphere Concentrations for Initial Syntactic-Foam Specimens Vs Manufacturer-Described Concentration.

Manufacturers' Description		Calculated Concentration	
Resin	Glass Microsphere Conc.		
	<u>% by Weight</u>	<u>% by Volume</u>	
Latex	10.0		18.5
Latex	23.0		54.0
Neoprene	4.2		3.2
Neoprene	8.5		14.0
Neoprene	17.5		5.7
Neoprene	27.6		21.5
PVC		50	5.7
Urethane		40	21.5
			6.2
			23.5
			36.0
			75.0
			13.0
			43.0

#### MATERIAL DEVELOPMENT

##### Purpose

Because of the limited number of manufacturers studying this problem area and the inclusiveness of conductivity results obtained on industry-developed material samples, NCTRU sponsored a material development with the Emerson and Cuming Company, a supplier of glass microspheres and a manufacturer of syntactic foams, to ascertain the influence of various material ingredients on final performance parameters. It was hoped that, by following a detailed development approach, one could either prepare an optimized material or extrapolate requirements for one. Also it was intended that any promising material sample would be prepared in sufficient quantity and size so that suits could be fabricated from the experimental material to verify thermal-conductivity values measured on material samples.

##### Concept

To develop a material which could overcome many of the limitations of foamed Neoprene at normal deep-sea depths, NCTRU decided to use the syntactic-foam approach that was utilized in some of the originally evaluated specimens. The replacement of the gas cells in foam materials with low-thermal-conductance incompressible particles seemed to be a proper approach. This technique had been used in the past principally to produce rigid materials for flotation and other applications. The NCTRU development objective was to obtain or produce a syntactic-foam material that was flexible and drapeable enough to be used in a swimsuit.

Since previous applications of syntactic foams were not as insulation, but as low-density fillers, little information on thermal-conductivity values were available on these composites. Thus, a thermal model was created to establish the apparent thermal conductivity for such a material. Figure 2 depicts the thermal model of this material composite.

The model shows the particles equally distributed and of equal size in the resin matrix with particle rows both in line with one another and separated. Since NCTRU assumed that the particles had a lower effective thermal conductance than the resin, this orientation of particles rather than the use of staggered rows would produce a more conservative (higher) thermal-conductance value for the composite. This configuration would permit a maximum particle volume of 52% when  $\ell = 2R$  (Figure 2). This particle concentration limit seemed appropriate since concentrations less than this would be required to achieve suitable flexibility and to prevent shattering of brittle particles because of high-contact stresses.

#### Derivations

Referring to Figure 2, the following heat flux expressions can be written:

$$Q = \frac{k_a \ell^2 (T_1 - T_3)}{\ell} \quad \underline{1}$$

$$Q = \frac{k_r \ell^2 (T_1 - T_2)}{\ell - 2R} \quad \underline{2}$$

$$Q = \frac{[k_r (\ell^2 - \pi R^2) + k_p \pi R^2] (T_2 - T_3)}{2R} \quad \underline{3}$$

Combining 2 and 3

$$Q = \frac{k_r \ell^2 [k_r (\ell^2 - \pi R^2) + k_p \pi R^2] (T_1 - T_3)}{k_r 2R\ell^2 + (\ell - 2R) [k_r (\ell^2 - \pi R^2) + k_p \pi R^2]} \quad \underline{4}$$

Combining 1 and 4

$$k_a = \frac{k_r \ell [k_r (\ell^2 - \pi R^2) + k_p \pi R^2]}{k_r 2R\ell^2 + (\ell - 2R) [k_r (\ell^2 - \pi R^2) + k_p \pi R^2]} \quad \underline{5}$$

$k_a$  = apparent thermal conductivity of composite

$k_r$  = thermal conductivity of resin

$k_p$  = thermal conductivity of particle taken as a cylinder composed of resin, shell material, and void material

$R$  = radius of spherical particle

$\ell$  = length of the sides of a cube representing the heat transfer geometry

Since  $V_p$  (Volume particle) =  $\frac{4}{3} \pi R^3$

$$R = .62 V_p^{1/3}$$

$$V_t \text{ (total Volume)} = \ell^3 = V_r \text{ (Volume resin)} + V_p$$

$$\ell = (V_r + V_p)^{1/3}$$

Substituting in 5

$$k_a = \frac{k_r \left[ k_r - 1.21 (k_r - k_p) \left( \frac{V_p}{V_r + V_p} \right)^{2/3} \right]}{k_r + (k_r - k_p) \left( \frac{V_p}{V_r + V_p} \right) \left[ 1.5 - 1.21 \left( \frac{V_r + V_p}{V_p} \right)^{1/3} \right]} \quad \underline{6}$$

If  $V_p$  is express as a fraction of  $(V_r + V_p)$

$$k_a = \frac{k_r \left[ k_r - 1.21 (k_r - k_p) V_p^{2/3} \right]}{k_r + (k_r - k_p) V_p \left[ 1.5 - \frac{1.21}{V_p^{1/3}} \right]} \quad \underline{7}$$

Before equation 7 can be applied an expression for  $k_p$  must be obtained.

Referring to Figure 1 again

$$Q = Q_1 + Q_2 \quad \underline{8}$$

$$Q_1 = \frac{k_p \pi R^2 (T_2 - T_3)}{2R} \quad \underline{9}$$

$$Q_1 = \frac{k_1 \pi R^2 (T_2 - T_2')}{t} \quad \underline{10}$$

$$Q_1 = \frac{k_2 \pi R^2 (T_2' - T_3')}{2(R - t)} \quad \underline{11}$$

$$Q_1 = \frac{k_1 \pi R^2 (T_3' - T_3)}{t} \quad \underline{12}$$

Combining 9 thru 12

$$k_p = \frac{2R k_1 k_2}{2(R-t) k_1 + 2tk_2} = \frac{k_2}{\frac{(R-t)}{R} + \frac{t}{R} \frac{k_2}{k_1}} \quad \underline{13}$$

$k_1$  = conductivity of particle cylinder from 0 to  $t$  and from  $2R-t$  to  $2R$

$k_2$  = conductivity of particle cylinder from  $t$  to  $2R-t$

since  $R$  is typically much larger than  $t$ , i.e.,  $R = 40u$ ,  $t = 2u$  and  $k_1$  is composed of glass and resin and  $k_2$  is composed of glass, resin, and void, such that  $k_g > k_r > k_v$ . Thus  $k_2 < k_1$

equation 13 can be simplified to:

$$k_p = k_2 \quad \underline{14}$$

Thus, only the interval from  $t$  to  $2R-t$  need be described with the other intervals treated as having no appreciable thermal resistance. Therefore,  $Q_1$  can be expressed as:

$$Q_1 = - \left\{ k_r \pi \left[ R^2 x - x(2R - x) \right] + k_g \pi t(2R-t) + k_v \pi \left[ x(2R-x) + t(t-2R) \right] \right\} \frac{dT}{dx} \quad \underline{15}$$

where  $t$  = shell thickness

$$- \int_{T_2}^{T_3} \frac{dT}{Q_1} = \int_0^{2R} \frac{dx}{\pi R^2 k_r + \pi t(2R-t)(k_g - k_v) - 2\pi R(k_r - k_v)x + \pi(k_r - k_v)x^2} \quad \underline{16}$$

Integrating 16

$$\frac{T_2 - T_3}{Q_1} = \frac{2}{\sqrt{q}} \left\{ \tan^{-1} \left( \frac{2\pi R(k_r - k_v)}{\sqrt{q}} \right) - \tan^{-1} \left( \frac{-2\pi R(k_r - k_v)}{\sqrt{q}} \right) \right\} \quad \underline{17}$$

$$\sqrt{q} = 2\pi \sqrt{(k_r - k_v) \left[ R^2 k_v + t(2R-t)(k_g - k_v) \right]} \quad \underline{18}$$

from 9

$$\frac{T_2 - T_3}{Q_1} = \frac{2R}{\pi R^2 k_p} = \frac{2}{\pi R k_p} \quad \underline{19}$$



Substituting 19 in 17

$$\tan \left( \frac{\sqrt{q}}{\pi R k_p} \right) = \frac{4\pi R \sqrt{q} (k_r - k_v)}{q - 4\pi^2 R^2 (k_r - k_v)^2} \quad \underline{20}$$

or since  $\tan x = -\tan(\pi - x)$

$$\tan \left( \frac{\pi - \sqrt{q}}{\pi R k_p} \right) = \frac{4\pi R \sqrt{q} (k_r - k_v)}{4\pi^2 R^2 (k_r - k_v)^2 - q} \quad \underline{21}$$

Rewriting 21

$$k_p = \frac{\frac{\sqrt{q}}{\pi R}}{\pi - \tan^{-1} \left( \frac{4\pi R \sqrt{q} (k_r - k_v)}{4\pi^2 R^2 (k_r - k_v)^2 - q} \right)} \quad \underline{22}$$

Substituting 18 in 22

$$k_p = \frac{\frac{2}{R} \sqrt{(k_r - k_v) [R^2 k_v + t(2R - t) (k_g - k_v)]}}{\pi - \tan^{-1} \left( \frac{2\sqrt{(k_r - k_v) [R^2 k_v + t(2R - t) (k_g - k_v)]}}{\frac{R(k_r - 2k_v) + t(2 - \frac{t}{R}) (k_g - k_v)}{R}} \right)} \quad \underline{23}$$

Data on particles from manufacturer indicate that particle thickness approximately changes with particle size to maintain particle density constant

$$\frac{4}{3} \pi (R^3 - R_2^3) P_{\text{shell}} = \frac{4}{3} \pi R^3 P_{\text{particle}}$$

$P_{\text{shell}}$  and  $P_{\text{particle}}$  are the density of glass and particle, respectively.

$$R^3 - R_2^3 = \frac{P_{\text{particle}} R^3}{P_{\text{shell}}}$$

$$P_{\text{shell}} = 162 \text{#/ft}^3 \quad P_{\text{particle}} = 16.6 \text{#/ft}^3$$

$$R_2^3 = R^3 \left( \frac{1 - 16.6}{162} \right)$$

$$R_2 = .965R$$

$$R_2 = R - t$$

$$R - t = .965 R$$

$$t = .035R$$

24

Substituting 24 in 23

$$k_p = \frac{2\sqrt{(.931 k_v + .07 k_g) (k_r - k_v)}}{\pi - \tan^{-1} \left( \frac{2\sqrt{(.931 k_v + .07 k_g) (k_r - k_v)}}{k_r + .07 k_g - 2.07 k_v} \right)} \quad 25$$

For glass  $k_g = .45 \text{ BTU/hr ft}^\circ\text{F}$

Substituting for  $k_g$  in 25

$$k_p = \frac{2\sqrt{(.931 k_v + .031) (k_r - k_v)}}{\pi - \tan^{-1} \left( \frac{2\sqrt{(.931 k_v + .031) (k_r - k_v)}}{k_r - 2.07 k_v + .031} \right)} \quad 26$$

The following is an assessment of  $k_v$ . The glass microballoons are formed at a temperature around  $2000^\circ\text{F}$  in air at atmospheric pressure and are cooled in room temperature ( $70^\circ\text{F}$ ). At room temperature the internal microballoon pressure can be estimated as:

$$P_i = \frac{T_2}{T_1} P_1$$

$$P_i = P \text{ internal (mm of Hg)}$$

$$P_1 = 760 \text{ mm of Hg}$$

$$T_2 = 70 + 460 = 530^\circ\text{F Abs.}$$

$$T_1 = 2000 + 460 = 2460^\circ\text{F Abs.}$$

$$P_i = \frac{530}{2460} (760) = 164 \text{ mm of Hg} = .164 \times 10^6 \mu \text{ of Hg}$$

Mean free path for air molecules ( $\lambda \text{ air}$ )

$$\lambda \text{ air} = \frac{5}{P_i} \times 10^4 \text{ u (Reference (2))}$$

$P_i \text{ in } \mu \text{ of Hg}$

$$\lambda \text{ air} = \frac{5 \times 10^4}{.164 \times 10^6} = .305 \text{ u}$$

$$\text{Dia Particle} = 80 \text{ u}$$

Since the mean free path of the molecule at the particle internal pressure is much smaller than the particle size, molecular collisions will control heat transfer through the particle and thus conductivity will be independent of pressure (2). It can, therefore, be assumed that  $k_v$  is approximately equal to .014 which is the thermal conductivity value for air at normal temperatures. Then substituting for  $k_v$  in 26

$$k_p = \frac{.423\sqrt{k_r - .014}}{\pi - \tan^{-1}\left(\frac{.423\sqrt{k_r - .014}}{k_r + .002}\right)} \quad \underline{27}$$

Equation 27 and 7 can be used to determine the influence of  $k_r$  and the volume % of spheres and resin on the apparent conductivity ( $k_a$ ) of the composite. Figure 3 shows the influence of  $k_r$  on  $k_p$  for the span of  $k_r$  shown. Equation 27, as can be seen from Figure 3 can be approximated as:

$$k_p = .015 + .445 k_r \quad \underline{28}$$

substituting 28 in 7

$$k_a = \frac{k_r \left[ k_r - (.67 k_r - .018) V_p^{2/3} \right]}{k_r + (.555 k_r - .015) \left( 1.5 - \frac{1.21}{1/3} \right) V_p} \quad \underline{29}$$

Since practical values for  $V_p$  range from 0 to .5 the expression

$$(.555 k_r - .015) \left( 1.5 - \frac{1.21}{1/3} \right) V_p \quad \text{from } \underline{29}$$

is at least one order of magnitude less than  $k_r$ ; thus, 29 can be further simplified to:

$$k_a = k_r - (.67 k_r - .018) V_p^{2/3} \quad \underline{30}$$

Figure 4 shows curves for  $k_a$  for a  $k_r$  range of .04 to .10 and a  $V_p$  range of from .2 to .5. The curves indicate that, to approach the thermal insulation of uncompressed neoprene foam, resin conductivities of less than .06 are required. As expected, the curves also indicate that as the resin conductance approaches the particle conductance the influence of particle volume on  $k_a$  decreases.

## Major Experimental Considerations

When the material development of the flexible syntactic foam was conducted, the following characteristics were used in judging the materials.

**Thermal Conductivity** - Since thermal conductivity has to be reduced as much as possible, the selections of basic resins, plasticizers, and the type of microspheres, all of which influence this property, had to accommodate this requirement.

**Drapeability** - The intention was to attempt to develop a material with the drapeability of Neoprene foam.

**Compressibility** - The material, to be considered acceptable, had to have good compression resistance ( i.e., less than 10%) to depths of 1000 FSW.

**Weight** - The only criterion for weight was that the material be light enough so that suits fabricated from the material would permit maneuvering out of water and that the material not be more dense than water.

**Water Retention** - The material should be impervious to water at all diving pressures.

## Sample Preparations

The material development was carried on in three phases (3).

The development included the study of various material composite ingredients and concentrations with the expectation of producing an optimized material using the syntactic-foam approach.

NCTRU evaluated the more promising systems primarily for Cenco Fitch thermal conductivity, compressibility, water absorption, and low-temperature drapeability characteristics. When final material selections were made, the scope of testing was expanded to include thermal conductivity under simulated deep-sea conditions, burst strength, abrasion resistance, loss of plasticizer, chemical resistance, flammability characteristics, weight loss at elevated temperatures, tensile strength elongation characteristics, stretch-flex properties, outgassing properties, and helium compatibility. A Unit-designed Hydrospace Simulator Facility (Figure 5) was used to determine some of the above-mentioned material properties where depth simulation was necessary.

The final material system selected was manufactured in sheets large enough that a swimsuit using standard wet-suit patterns could be fabricated for material thermal-conductivity evaluation. A suit was also fabricated for the same purpose from the proprietary, vinyl, syntactic-foam material which was also being improved during the period of this development.

The material components considered under this program were:

#### Resins

- Polyurethane
- Styrene Acrylonitrile
- Polypropylene
- Chlorinated Polyether
- Polystyrene
- Polyvinylidene Fluoride
- Natural Rubber
- Butyl Rubber

#### Plasticizers

- Diethylphthalate
- Aroclor 1254
- Fyrgwel 220
- Diisodecyl Adipate
- Hydrocarbon HB40

#### Low-Density Fillers

##### Hollow-Glass Spheres

- Type IG 101 - made from Sodium borosilicate glass
- Type FT 102 - glass having better water insolubility than IG 101

##### Ceramic Spheres

- Type SI shell composed of silicone dioxide

##### Plastic Spheres

- UFO - shell composed of urea formaldehyde
- Saran shell material

#### Sample Materials

The resins were selected for study because of their low, published, thermal-conductivity values. Of these resins only a low molecular-weight butyl and the polyurethanes were considered suitable for further study because the others would not lend themselves to the heavy plasticization that this application would require (3).

Production of sample materials from the butyl resin, a castable two-part Urethane compound, referenced as CPC-41, and seven other Urethane compounds made from Dupont Urethane resin Adiprene C-167 and crosslinkers of glycerine, hexane diol, hexane triol, Polyol 220, Puracel 2010, Puracel 1010, and Polyol 245 with heavy amounts of plastizers to achieve good drapeability culminated in the selection of the CPC-41 Urethane as the most promising component (3).

The initial material samples were unfilled, unplasticized CPC-41 polyurethane resin, and unplasticized CPC-41 with glass, glass and plastic, and plastic hollow spheres to determine the lowest thermal-conductivity properties possible with these systems. Table III contains thermal conductivity data for these samples.

TABLE III. Thermal Conductivity Data for Various Concentrations of Different Particle Types with One Resin Matrix

Sample No. Resin	Type of Particle	Part. Conc. (% by Volume) *	Density #/ft <sup>3</sup>	Cenco Fitch Thermal Conductivity BTU/hr ft °F
1. CPC 41	none	0	84.2	0.104
2. CPC 41	glass	58	45.0	0.099
3. CPC 41	glass & plastic	--	35.8	0.080
4. CPC 41	plastic	64	35.3	0.058
5. CPC 41	plastic	86	18.7	0.047

\* Calculated

The particle concentrations were computed assuming particle densities of 16.6#/ft<sup>3</sup> for glass and 8#/ft<sup>3</sup> for plastic spheres. These data indicate that glass particles do not lower thermal-conductivity properties, but plastic particles are very effective in this regard. This fact did not seem completely plausible considering the results obtained from theoretical work. Theoretical computations restricted concentrations to below 50% by volume because of possible particle contact with resultant breakage. If breakage occurred, there would be solid-glass particles as well as hollow spheres in the matrix. This would then seriously compromise the conductivity value achieved since glass has a high thermal conductivity (.45 BTU/hr ft° F). Because plastic deforms rather than shatters when in point contact under stress, no severe compromise in thermal conductivity would be expected for these types of particles. As can be seen from Table III, significant conductivity reductions were obtained with plastic particles as concentration increased, which tends to support the observation that some fracture of glass particles occurs when these material samples are compounded.

Initial Development Samples. Similar samples of the materials shown in Table III were submitted to NCTRU for study to guide future development efforts. The data obtained on these samples as well as their descriptions are given in Table IV.

Table IV. Composition and Performance Data on Initial Development Samples

Sheet Code	Material Composition (% by Wt)				Den- sity #/ft <sup>3</sup>	Thick- ness Change 1000 FSW(%)	Cenco Fitch Thermal Cond. BTU/hr ft <sup>2</sup> °F
	Resin	Plasticizer	Particles				
	CPC-41	Diethyl- phthalate (DOP)	Glass	Plastic			
WS01	75.4	6.3	18.3	0.0	44.9	0.7	.080
WS01a	75.4	6.3	18.3	0.0	44.9	0.8	.082
WS02	80.0	6.6	12.5	1.9	35.8	7.9	.063
WS03	88.5	7.4	0.0	4.1	35.3	12.0	.057
WS30	87.0	0.0	0.0	13.0	17.6	23.7	.038
WS31	81.2	6.6	0.0	12.2	17.4	19.8	.035

The only difference in composition between the Table III and IV samples was the addition of a bit of plasticizer. However, all of the glass-loaded samples in Table IV tended to show lower thermal-conductivity values than those given in Table III. Figure 6 plots the thermal conductivity data in Table III and IV versus material density. From Figure 6 it can be seen that there was a wide difference in measured thermal conductivity for the all-glass-loaded specimens of the two sample sets. The lower value obtained on the Table IV WS01 specimen seems to agree more closely with theoretical results. Figure 4 data would have predicted a  $k_g$  of .07 for the WS01 composition rather than the .08 measured for a  $k_r$  of .10. The data in Figure 6 also indicate the effect of particle shell material on thermal conductivity, the plastic achieving much lower values.

In going from a glass-plastic combination to an all-plastic-loaded composition, there was essentially a step change in thermal conductivity for the same material density although this change was less dramatic for the Table IV sample set. As was mentioned previously, the differences in conductivity for samples containing glass particles may have been associated with particle fracture. It may be that the addition of a plasticizer or lubricant in the Table IV set lowered the amount of breakage by reducing the friction between particles in contact with each other, thereby permitting slippage and achieving significant reductions in thermal conductivity with the addition of glass particles.

The Table IV data also indicate the compressive resistance of the various specimens listed. Thickness change at a depth of 1000 FSW went from less than 1% for the all-glass-loaded material to approximately 24% for the WS30 all-plastic-loaded material. From these data, WS03 was selected for further development as the best compromise choice for weight, thermal conductivity, compressibility, and flexibility. Flexibility, however, was somewhat irrelevant since all of these Table IV samples were stiff and unsuitable for swimsuit fabrication in their present form.

Second Sample Set. After some experimentation two more samples were prepared which were similar to the WS03 specimen except that the two basic ingredients of the CPC-41 Urethane were added in different concentrations from nearly 1:1 to 1:3 by weight to improve drape. Table V shows the data and composition on these two samples.

Table V. Composition and Performance Data on Second Sample Set

Sheet Code	Material Composition (% by Weight)				Density #/ft <sup>3</sup>	Thick Change @ 1000 FSW (%)	Cenco Fitch Thermal Cond. BTU/hr ft <sup>2</sup> °F	Drape at °F
	Resin CPC-41	Catalyst Amine	Particles Glass	Plastic				

WS32	93.4	2.0	--	4.6	33.6	33.3	.052	Stiff
WS36	93.5	1.9	--	4.6	33.2	39.0	.056	Stiff

Table VI. Composition and Performance Data on Third Sample Set

Sheet Code	Material Composition (% by Weight)				Density #/ft <sup>3</sup>	Thick Change @ 1000 FSW (%)	Cenco Fitch Thermal Cond. BTU/hr ft <sup>2</sup> °F	Drape at °F
	Resin CPC-41	Plasticizer DOP	Catalyst Amine	Particles Glass	Plastic			

III	66.8	27.3	1.2	--	4.7	38.6	36.0	.052	Stiff
IV	54.3	22.2	1.0	22.5	--	38.4	4.6	.070	Stiff
V	58.8	24.2	1.1	13.6	2.3	36.2	21.1	.059	Stiff
VI	49.4	22.6	1.0	27.0	--	36.0	4.6	.070	Stiff
VII	71.0	27.8	1.2	--	--	65.4	0.0	.085	Flex



Although the drape properties were improved in normal room temperatures and the change in composition in the CPC-41 did not appreciably change thermal conductivity, the composite did not maintain its flexibility at low temperature (0°F) but became stiff (Table V). The development of a flexible matrix for the plastic spheres also caused a severe increase in compressibility from 12% for WS03 to 33 to 39% for these specimens (Tables IV and V). Apparently, the stiffer matrix of the WS03 specimen provided the compressive support in that sample rather than the plastic spheres. As this matrix was made less rigid, the spheres were required to share more of the compressive support but did not have sufficient inherent strength to do so.

Third Sample Set. To substantiate this observation and improve low-temperature drape, five more specimens were prepared. One was similar in composition to the WS32 and WS36 except that about 27% of dioctylphthalate (DOP) plasticizer was added (Sheet III, Table VI); three of the others replaced the all-plastic particle filler with glass or glass and plastic, and all had DOP added. The fifth specimen represented the unfilled resin. Table VI lists the results obtained on these specimens as well as their composition.

As can be seen from Table VI, the high compressibility of the WS32 and WS36 specimens was repeated in specimen III. Specimen V, which also had plastic particles, compressed as much as 21% at 1000 FSW. Good compressible resistance was obtained only by the unfilled and all-glass-filled specimens. Thermal-conductivity data for the glass-filled systems were lower than obtained previously for the WS01 sample referenced in Table IV because of the lower resin  $k$ , greater fill concentration, and possibly less breakage because of higher plasticizer concentration. Reasonable drape at room temperature was also possible with these samples even with the higher glass concentration because of the larger amounts of plasticizer used. Low-temperature drapeability for all filled specimens was still poor but the unfilled specimen remained flexible even at 0°F. It became apparent at this time that: (a) plastic spheres were not suitable as filler because of their poor compression resistance although they showed low thermal conductivity and could be applied at lower pressures; (b) high concentrations of glass spheres would be needed to suitably lower material thermal conductivity and density; (c) to achieve low-temperature drapeability with a highly filled system, greater percentages of plasticizer would have to be used; and (d) an attempt should be made to minimize resin-plasticizer thermal conductivity as much as possible.

Fourth Sample Set. Nine more samples were prepared with CPC-41 resin with various plasticizers of different concentrations and the samples were examined for thermal conductivity and drape properties (Table VII).

From Table VII data it can be seen that the diisodecyl adipate specimen seemed to be the most promising because of its low-temperature flexibility and low weight. Dioctylphthalate and hydrocarbon HB-40 systems seemed equivalent, with the aroclor specimens being the worst. The aroclor samples became stiff at low temperature and had the highest density.

Table VII. Composition and Performance Data on Fourth Sample Set

Sheet Code	Materials Composition (% by Weight)		Density #/ft <sup>3</sup>	Cenco Fitch Thermal Cond BTU/hr ft <sup>2</sup> °F	Relative Drape (OOF)
	Resin CPC 41	Plasticizers Type			
TMC-VII	69.0	Diethylphthalate	31.0	.092	Stiff
TC-AI	64.6	"	35.4	.082	Very Flex
TMC-VIII	64.6	"	35.4	.093	Flex
TMC-IX	61.6	"	38.4	.092	Very Flex
TC-AV	78.4	Aroclor 1254	21.6	.085	Stiff
TC-AII	64.5	"	35.5	.079	Stiff
TC-AIV	64.5	Fyrgwel	35.5	.085	Stiff
TC-BIII	64.5	Diisodecyl Adipate	35.5	.084	Very Flex
TC-AIII	64.5	Hydrocarbon HB-40	35.5	.088	Flex

Fifth Sample Set. Further samples were made using the dioctylphthalate, diisodecyl adipate and hydrocarbon plasticizers with two types of glass and one type of ceramic sphere. The samples were tested for thermal conductivity, thickness compression, and low-temperature drapeability (Table VIII).

Table VIII data indicate that: (a) more plasticizer was still needed for low-temperature flexibility in all but the diisodecyl adipate sample; (b) the IG101 particles seemed to lower thermal conductivity most in dioctylphthalate specimens; and (c) highest thermal conductivity occurred in the diisodecyl adipate sample. This sample also had the highest glass loading (possible particle breakage). An additional diisodecyl adipate sample was made which showed a value of .08 for thermal conductivity. Subsequent investigation showed the surface of the TC-B111 (Table VII) to be non-uniform which would have affected the measured thermal-conductance values.

Water-absorption tests were also conducted on the A8/20 and C10/20 specimens at 1000 FSW. The A8/20 specimen gained only 0.5% in weight after 32 hours while the C10/20 specimen gained 11% after 72 hours. We suspected that this was due to poorer water-insolubility characteristics of the diisodecyl adipate plasticizer. Because of the high-water retention in the C10/20 sample, the diisodecyl adipate plasticizer was eliminated from further consideration.

Sixth Sample Set. Further experimentation to achieve more flexibility with either the dioctylphthalate or hydrocarbon HB-40 plasticizer revealed that the best flexibility could be obtained with systems containing CPC-41, FT102 glass spheres, and hydrocarbon HB-40 plasticizer (3). (Similar mixtures with IG101 particles did not cure completely.) Formulations with these ingredients were prepared containing equal volumes of FT102 particles in three different mesh ranges (Table IX).

The room-temperature drape of specimens A26FT-4 and A26FT-5 was better than that of the A26FT-3 specimen. Even these specimens, however, became boardy at 30°F and were very stiff at 0°F. Because the unfilled resin-plasticizer mix was flexible at 0°F, the only way to improve low-temperature flexibility was to reduce the glass-sphere loading. Thermal conductivity data in Table IX show that, for the particle size range investigated, thermal conductivity values were about the same and were about equal to the values obtained with lighter loads of these particles in a similar matrix material (shown in Table VIII) although the proportion of resin and plasticizer was essentially reversed. Even though the mesh size for the particles in the sample matrixes were substantially different, thermal-conductivity values were essentially unchanged. This agrees with previous theoretical considerations provided that the density of particles remains the same regardless of size (because shell thickness is a function of particle radius). This concept of constant density seems to be only approximately valid since particles in the 150-200 micron range and the 0-to-100 micron range were 16.5 and 6.5% heavier, respectively, than those encompassing the entire size range of 0 to 200 microns (Table IX). The density changes are relatively small, however, considering that the particle size range evaluated differed by at least 50 to 100% (0 to 100 microns to 150 to 200 microns). As can also be seen from

(continued on page 24)

Table VIII. Composition and Performance Data on Fifth Sample Set

Sheet Code	Material Composition (% by Weight)			Density #/ft <sup>3</sup>	Cenco Fitch Thermal Cond. BTU/hr ft °F	Thick Change 1000 FSW (%)	Relative Drape (°F)
	Resin Type	Conc.	Plasticizer Type	Particle Conc. Type Conc.			
A	CPC-41	61.1	Diethylphthalate	27.4 IGL01 11.5	.067	1.0	Stiff
B	CPC-41	61.2	"	27.6 FTL02 11.2	.081	3.0	Stiff
C	CPC-41	61.6	"	28.7 Si 9.7	.080	1.2	Stiff
A8/20	CPC-41	62.8	Hydrocarbon HB-40	31.2 FTL02 6.1	.084	-	Stiff
B8/20	CPC-41	62.3	"	31.0 FTL02 6.7	.080	-	Stiff
C10/20	CPC-41	57.7	Diisodecyl Adipate	29.4 IGL01 12.9	.093	2.4	Flexible

Table IX. Composition and Performance Data on Sixth Sample Set

Sheet Code	Material Composition (% by Weight)			Particle mesh microns	True particle density g/cc	Mate- rial density #ft <sup>3</sup>	Cenco Fitch Ther. Cond.	Low Temp Drape O°F
	Resin CPC-41	Plasticizer HB-40	Particle FT102					
A26FT-3	30.9	47.6	21.5	150-200	.289	38.8	.078	Stiff
A26FT-4	30.7	49.1	19.2	< 200	.248	39.0	.079	Stiff
A26FT-5	30.5	48.5	20.0	< 100	.264	38.0	.076	Stiff

Table X. Composition and Performance Data on Seventh Sample Set

Sheet Code	Material Composition (% by Wt)			Cure Temp (°F)	Den- sity #/ft <sup>3</sup>	Cenco Fitch Thermal Cond. BTU/hr	Thick Change @ 1000 FSW (%)	F L E X		
	Resin CPC-41	Plastici- zer HB-40	Particle					30°F	0°F	0°F
71/7B	55.8	31.0	13.2	R.T.*	44.2	.083	3.2	Flex	Stiffened Slightly	
71/7C RT	59.4	33.5	7.1	R.T.	51.3	.092	1.4	Flex	Stiffened Slightly	
71/73-150	59.4	33.5	7.1	150	51.3	.094	2.4	Stiffened Slightly	Stiff	
71/10A	57.4	32.4	10.2	R.T.	47.0	.088	2.6	Flex	Stiffened Slightly	

\* R.T. = Room Temperature

Table IX, the principal sample ingredient was plasticizer. Thus, attempts to improve drape considerably reduced the physical strength of the material because of the large additions of plasticizer.

Seventh Sample Set. Four more samples were produced reducing the FT102 concentration. Table X shows the composition and data obtained from these specimens.

From the Table X specimens the 71/7B sample seems to have the best measured properties, but its surface softened during the Cenco Fitch thermal-conductivity test (high temperature platen, 180°F). Thus 71/10A was selected as having the best overall properties for further development. Data on the 71/7C RT and the 71/73-150 showed that high-temperature cures tended to reduce material drapeability. Although the 71/10A was selected as the best sample, it still had poor inherent strength and stretch-recovery properties. The material had essentially a doughy consistency.

Eighth Sample Set. To impart strength, stretch and recovery properties to the materials, samples of Spandex-type materials having different load-elongation characteristics were cured to the surfaces of the 71/10A composition. Table XI gives the test data and description of these material samples.

Table XI. Composition and Performance Data on Eighth Sample Set

Property	Sheet Code		
	1	2	3
Thermal Conductivity (BTU/hr ft °F)			
Cenco Fitch	.085	.084	.090
Guarded Hot Plate	.091	.099	.106
Guarded Hot Plate @ 450 psi	.100	.100	.112
Water Retention (% by weight)	0.35	1.20	0.70
Low-Temperature Drapeability at 30°F	Stiffened Slightly	Stiffened Slightly	Flexible
0°F	Stiff	Stiff	Stiffened Slightly
Thickness Change at 450 psi (%)	2.3	1.6	2.0

1. Spandex Power-Net Fabric (2 lb loading-60% elong) on one side only.
2. Spandex Power-Net Fabric (2 lb loading-60% elong) on one side and a two-way, stretch-nylon knit on the other side.
3. Banlon knit material on both sides.

The best drapeability was obtained with the Banlon fabric. Table XI data also show variations in thermal-conductivity results depending on the measuring technique used. The guarded-hot-plate device, which was used to obtain thermal-conductivity data under simulated depth conditions, gave higher values.

It was felt at this point that any further experimentation with material composition or backing fabrics would only yield minor material improvements. Thus, the Banlon-knit material was selected for final sheet fabrication.

#### Final Evaluations

Large sheets of the 71/10A composition with Banlon-knit materials cured to the surfaces were obtained for more complete determinations of material properties and for suit fabrication so that thermal-conductivity data taken from the samples could be verified. Large sheets of an industrially developed PVC-glass-microsphere composite material were also purchased to obtain information comparable with that for the Urethane glass-microsphere composite (71/10A composition). In addition to these materials the proprietary, polymerized, oil-glass, microsphere material already tested by other Navy agencies was investigated for outgassing and helium-compatibility characteristics. The currently used, Neoprene-foam material was also subjected to the same test series for comparison purposes.

#### MATERIAL TESTS

##### Parameters

The methods of test used in evaluating the final materials are described in Appendix A. The following lists the material properties determined for both the Urethane and the PVC composites.

- (a) Thickness
- (b) Thickness Change at 1000 FSW
- (c) Density
- (d) Thermal Conductivity at depths down to 1000 FSW
- (e) Burst Strength
- (f) Abrasion Resistance
- (g) Chemical Resistance to Selected Reagents
- (h) Drape Stiffness
- (i) Water Retention @ 1000 FSW
- (j) Flammability under Normal Atmospheric Conditions
- (k) Weight Loss Data at Elevated Temperatures
- (l) Strength-Elongation Properties
- (m) Outgassing Properties
- (n) Helium Compatibility @ 1000 FSW
- (o) Stretch-Flex



Table XII. Test Results of Potential Deep-Sea Swimsuit Materials

## MATERIAL

	Urethane Comp(1)		Vinyl Composite(2)			Neoprene Foam(3)		
	Normal Atm.	1000 FSW	Normal Atm.	1000 FSW	Normal Atm.	Normal Atm.	20 FSW	1000 FSW
Thickness (in)	.354	.346	.245	.240	.345	.285	.235	.176
Thickness Change (%)		2.5		2.0			21.0	62.0
Conductivity Cenco Fitch BTU/hr ft °F	.080		.072		.075	.038		
Thermal Conductivity Guarded Hot Plate BTU/hr ft °F	.096	.108	.100		.100	.046	.092	.251
Specific Weight #/ft <sup>3</sup>	45.4		52.5			19.1		31
Burst Press. (psi)	66		115		123	94		
Abrasion Resistance (4)	8000+		534		400	390		
Drape Stiffness (psi) @ 50°F @ 20°F @ 0°F	14.3 28.2		23.9 24.4 25.4		23.2 27.8 28.6	37.4 41.4 44.9		
Water Pick-up after 24 hrs @ 1000 FSW (%)	3.5		6.5		6.5	16		

Table XII. (Cont'd)

Flammability	continues to burn after removal of ignition source until material consumed	same as urethane normal	same as urethane normal	continued to burn for 40 sec after removal of ignition source
Loss of Wt after oven aging for 14 days (%) @ 110°F @ 140°F @ 175°F	1.35 4.04 10.95	1.75 2.56 3.30	1.75 2.56 3.30	4.15 5.75 8.88
Tensile Strength (psi) Elongation (%)	155 336	280 238	145 236	153 258
Flex-Stretch a) Disp (in) b) Diff Press (in H <sub>2</sub> O)	.113 23	.129 20	.138 23	.272 23

## NOTES

- (1) Urethane Composite - Experimental swimsuit material formulated for NCTRU under contract.
- (2) Vinyl Composite - Proprietary material.
- (3) Neoprene Foam - Standard foam material used in the manufacture of conventional wet-style swimming suits.
- (4) Abrasion resistance - Failure No. of cycle before backing material was penetrated.

## Results

A summary of the test results obtained on the Neoprene foam and the Urethane and PVC composites is given in Table XII. Chemical resistance, helium compatibility, and outgassing characteristics, which are not shown in this table, are discussed separately.

Table XII data show that both the Urethane and the PVC materials showed very little compressibility at 1000 FSW (2.5% or less) as compared with Neoprene foam (62%). Neoprene foam had about one-half of the thermal conductivity of the other two materials at normal atmospheric pressure but this advantage was lost once a depth of 20 FSW was reached. Moreover, at 1000 FSW, the Urethane and vinyl thermal conductivities remained essentially the same as at normal atmospheric pressure and were less than one-half the Neoprene-foam value at this depth.

The specific weight of the Neoprene foam at normal atmospheric pressure was substantially lower than the other materials, but at 1000 FSW its specific weight increased more than 50%. The PVC material, which was about 15% heavier than the Urethane, had the best burst strength characteristics. The tensile strength of the thicker PVC samples was essentially equivalent to the Urethane and Neoprene. The thinner PVC had considerably more tensile strength than the others.

A comparison of the strength elongation data showed that the Urethane material had the lowest modulus, the Neoprene and thicker PVC specimen were approximately the same, and the thinner PVC was the highest. The flex-stretch data showed the Neoprene to be considerably superior to the other materials and the PVC somewhat better than the Urethane. The Urethane showed the lowest water retention with the Neoprene being considerably worse than the others. All had poor flammability characteristics but all showed rather low volatility (determined by weight loss) up to 140°F, but at 175°F, both the Urethane and Neoprene materials had considerably higher weight losses than the PVC. The Urethane showed the best abrasion resistance primarily because of the better adhesion and protection that the backing material provided the Urethane in comparison with the others. The drape stiffness of both the Urethane and vinyl materials was superior to the Neoprene foam down at 20°F. At 0°F the PVC still had the best drape properties of the three materials and the Urethane had stiffened sufficiently at this temperature so that the property could not be measured objectively. As was pointed out previously, the Cenco Fitch thermal-conductivity data produced lower results than the guarded hot-plate data.

Chemical Resistance. The effect of various chemical reagents on the sample materials is shown in Table XIII. All of the materials were affected in varying degrees, from rather small weight gains or losses to complete decomposition, depending on the nature of the acid, solvent, or hydrocarbon. Reagents, such as kerosene and motor oil, which could be expected to be found in use in a diving operation, had less effect on the Urethane composite. Both the PVC and Neoprene materials showed considerable weight changes for these reagents, primarily for the kerosene (approximately 44%). For the 10% NaCl solution (salt water) the Neoprene showed the greatest weight change and the Urethane the least.

Table XIII. Effect of Various Chemicals on Deep-Sea Divers' Suit Materials  
(Based on ASTM Test Method D543)

Reagent	Material	% Wt Loss	% Wt Gained	% Area Loss	% Area Gained	Chemical Effort
Glacial Acetic Acid SpG 1.05	Neoprene		70.4	26.5		Slight swelling
	Vinyl Composite	40.8			34.0	Shrinkage
	Urethane Composite		41.9	12.8		Stiffening
5% Sol. Acetic Acid	Neoprene		56.3	26.5		Slight swelling
	Vinyl Composite		15.5			No effect
	Urethane Composite		9.5			Slight tackiness
Acetone	Neoprene		39.1			No effect
	Vinyl Composite		37.1	56.0		Swells and cracks
	Urethane Composite					Decomposition
Concentrated Ammonium Hydroxide	Neoprene		23.1			No effect
	Vinyl Composite		41.9			No effect
	Urethane Composite		4.3			Tackiness
Aniline	Neoprene		61.9	26.5		Slight swelling
	Vinyl Composite	14.3			23.0	Slight shrinkage
	Urethane Composite		65.9	56.0		Much swelling
Benzene	Neoprene		73.4	28.7		Tackiness
	Vinyl Composite					Slight decomposition
	Urethane Composite					Stiffening
10% Sol. Citric Acid	Neoprene		24.9			Swelling
	Vinyl Composite		9.3		34.0	Rubbery
	Urethane Composite		5.8			Stiffening
						Decomposition
						No effect
						No effect
						No effect

Table XIII. Continued

Heptane Commercial Grade B.P. 98° to 100°C	Neoprene	50.3	12.8	43.75	Slight swelling
	Vinyl Composite	53.4			Shrinkage
	Urethane Composite	0.7			Stiffening
Concentrated HCl	Neoprene				No effect
					Consumed backing material
	Vinyl Composite				Consumed backing material
Methyl Alcohol	Urethane Composite				Decomposition
	Neoprene	42.9	26.5	12.0	Slight swelling
	Vinyl Composite	23.9			Stiffening
	Urethane Composite	9.5	12.8		Shrinkage
					Swelling
					Much tackiness
Mineral Oil	Neoprene	11.9			No effect
	Vinyl Composite	14.0		12.0	No effect
	Urethane Composite	17.4			No effect
Kerosene	Neoprene	59.5	12.8	34.0	Slight swelling
	Vinyl Composite	44.1			Shrinkage
	Urethane Composite	5.8			Stiffening
30 SAE Motor Oil	Neoprene	13.6			No effect
	Vinyl Composite	7.6		12.0	Slight swelling
	Urethane Composite	1.4		20.1	Slight stiffening
5% Phenol Sol.	Neoprene	33.7			Tackiness
	Vinyl Composite				No effect
	Urethane Composite	17.9			No effect
2% Sodium Carbonate Sol.	Neoprene	14.2			No effect
	Vinyl Composite	25.5			No effect
	Urethane Composite	3.4			No effect
		4.8	12.8		Slight swelling
					Slight tackiness

Table XIII. Continued

Reagent	Material	% Wt Loss	% Wt Gained	% Area Loss	% Area Gained	Chemical Effort
10% Sodium Chloride	Neoprene		22.1			No effect
	Vinyl Composite		6.7			No effect
	Urethane Composite		1.8			No effect
JP-4	Neoprene		60.5	26.5		Slight swelling
	Vinyl Composite	44.0			38.9	Shrinkage
	Urethane Composite					Stiffening
Glycerin	Urethane Composite		7.3			Slight swelling
	Neoprene		20.0			No effect
	Vinyl Composite					No effect
Oleic Acid	Urethane Composite					No effect
	Neoprene		56.4	26.5		Slight swelling
	Vinyl Composite	21.8			23.4	Hardening
Toluene	Urethane Composite		18.7	6.4		Slight swelling
	Neoprene		81.2	97.7		Tackiness
	Vinyl Composite					Swelling
Perchlor ethylene	Urethane Composite				17.9	Rubberiness
	Neoprene		87.2	89.1		Stiffening
	Vinyl Composite	18.0			34.0	Decomposition
Carbon Tet.	Urethane Composite		73.3	48.5		Swelling
	Neoprene		88.5	87.0		Tackiness
	Vinyl Composite	31.7			43.8	Rubberiness
	Urethane Composite		75.0	26.5		Much swelling
	Neoprene					Shrinkage
	Vinyl Composite					Much stiffening
	Urethane Composite					Slight decomposition
	Neoprene					Rubberiness
	Vinyl Composite					Much swelling

Helium Compatibility. The PVC and Urethane materials were tested to determine the effect on their properties of exposure to helium gas at 1000 FSW. The samples were subjected to the helium atmosphere for 24 hours. Upon release of pressure, examination of the specimens indicated that the vinyl material was not affected in any way. However, some of the helium gas which had permeated the Urethane material under pressurization failed to be released and produced a thickness growth of from 0.381" to 0.651" (71% increase). This gas could be removed only by placing the material in a vacuum chamber where it returned to its original thickness. Prior to gas removal in a vacuum chamber, the sample had undergone a second pressurization and depressurization cycle which caused recompression of the sample to within 0.004" of its original thickness and reexpansion upon depressurization to 0.651". Thus, there was no further gain in the amount of gas trapped.

This entrapped gas condition was not peculiar to helium but also occurred with compressed nitrogen.

The normal material state for the Urethane is somewhat tacky and, based on the growth experienced with this material, it appears that this adhesive quality permits the sample to trap gases when the differential pressure between the sample and its surroundings becomes less than one atmosphere. Because the vinyl material does not have this tacky quality, no gas is trapped, and no growth occurs upon depressurizing. This effect can be expected from any material which has this tacky, gum-type characteristic. In fact, a sample of a polymerized-oil, glass-microsphere material which is also tacky in nature was similarly checked and sample growth also occurred with this material.

Outgassing Characteristics. Samples of the Urethane, PVC, and polymerized oil materials were subjected to vacuum distillation at 95°F to determine what volatile compounds, if any, could be collected from the specimen. Analysis was performed by combined gas chromatographic and mass spectrometric methods. Collection periods of 6 hours were used at 1 micron of the Hg pressure and 95°F. (These tests were conducted for this Unit by Pioneering Research Laboratory, U. S. Army Natick Laboratories.) Results of these tests indicated that no compounds other than ordinary air were detected in concentrations greater than 1 part per million. It would appear from these results that any of these materials would not normally cause a toxic hazard while being stored in diving chambers since, under the high pressures maintained in these diving habitats, outgassing effects would be even less.

#### SWIMSUIT FABRICATION AND EVALUATION

Three swimsuits of the wet-suit style were fabricated--one from the Urethane material and one each from the two different thicknesses of the PVC. It became apparent that the bulk and weight of these materials would make fabrication more difficult than was experienced with Neoprene foam. A good cemented seam could not be obtained with either the PVC or the Urethane materials. The Urethane material caused further bonding difficulties because it has, as mentioned previously, a doughy consistency and poor inherent strength. To overcome these problems and to expedite the manufacture of these suits, all pieces were mechanically held together by hand stitching before cementing. All joints were then cemented and taped on both sides to

provide additional strength. This exercise highlighted the special fabrication and suit-design problems that will be encountered with these materials to obtain a functional, durable, and economical suit configuration. Since establishing this design was not the intent of this materials development, no effort was expended in this regard.

The Urethane and vinyl suits, along with a standard-style, Neoprene-foam wet suit, were tested for thermal-conductivity properties on an instrumented, heated, copper manikin submerged in water at 1 FT of H<sub>2</sub>O pressure to verify sample thermal-conductivity information. (These tests were conducted for this Unit by the Military Ergonomics Laboratory, U. S. Army Research Institute of Environmental Medicine (USARIEM), U. S. Army Natick Laboratories.) Figures 7, 8, 9, and 10 show the Urethane and vinyl suits on the manikin prior to and after submergence of the dressed manikin in the ARIEM pool. There was no water circulation other than convective effects. Table XIV shows the thermal-conductivity data obtained on the various suits as well as other suit properties.

Table XIV. Thermal-Conductivity Data for Wet-Style Swimsuits  
Fabricated from Standard and Experimental Materials

Suit material	Material thickness (in)	Effective suit thickness (in)	Suit weight (lbs)	Material thermal conductance uncorrected BTU/hr ft <sup>2</sup> °F	Material thermal conductance corrected BTU/hr ft <sup>2</sup> °F	Material thermal conductance corrected BTU/hr ft <sup>2</sup> °F
Nude Manikin	--	--	--	9.44	--	--
Neoprene Foam	.250	.31	10	1.56	1.87	.048
PVC	.250	.34	30	2.64	3.65	.102
PVC	.375	.49	44	2.15	2.78	.114
Urethane	.375	.53	41	1.87	2.36	.104

Before Table XIV conductance data is considered, the item labeled effective suit thickness needs to be explained. When a wet suit is worn, there are overlapping material areas such as at the shoulder, chest, wrist, ankles, and from the hips to the middle of the torso. Therefore, use of the basic material thickness tends to project a material conductivity which is lower than it actually is. An effective thickness was computed for each suit from available suit weight, material specific weight, and manikin surface area data. Thus, more correct thermal-conductivity data could be estimated. The difference between the corrected and uncorrected thermal-conductance data shown in Table XIV was the elimination of the convective-heat-transfer skin



coefficient that persists in all of the uncorrected data. This coefficient is exactly equal to the nude-manikin, thermal-conductance value. The corrected thermal-conductivity values more closely agree with the guarded-hot-plate data of Table XII. The data for Neoprene foam, vinyl, and Urethane agree with sample test data within 5 to 14%. Cenco Fitch agreement range from 21 to 34% for these same materials. These corrected data show that Cenco Fitch and guarded-hot-plate conductivity values are both useful for screening purposes with the guarded-hot-plate providing the more accurate information. The degree of agreement obtained between the sample, guarded-hot-plate, thermal-conductivity data and the copper-manikin data indicated the suitability of using sample conductance data to predict suit performance.

## DISCUSSION OF RESULTS

Thermal-conductivity data obtained throughout the development cycle as well as determined on the final materials does not approach the lower values predicted theoretically. As discussed previously, this suggests that the utilization of glass spheres causes some particle destruction when the material is compounded, a result which negates to some extent the degree to which the thermal conductivity is lowered. This assumption is substantiated to some degree by the substantial reductions in thermal conductance that were obtained in samples loaded with unbreakable plastic spheres. Because of this, it is believed that thermal-conductivity was not lowered as much as what should be expected for the particluar loadings obtained in the final samples.

The final composition of the Urethane material resulted from an attempt to balance the influence of the different composite ingredients on the final product. Higher loadings would have been possible if the low-temperature drape criteria had been relaxed considerably. For shallower depth applications, using plastic instead of glass spheres would permit the attainment of a lower weight and thermal conductivity.

The heavy plasticization required to attain suitable drape even at normal room temperatures with these types of fillers suggests that the final composite would require some sort of backing material to provide strength, stretch, and recovery.

The final results on the experimental PVC and Urethane materials indicate that both are suitable for incompressible swimsuit materials because both have similar compressibility, thermal conductivity, flammability, stretch-flex, and outgassing properties. The PVC has better low-temperature drape properties but the Urethane has better room-temperature drape properties. The Urethane is less dense than the vinyl and has a lower modulus (less resistance to elongation) to aid movement, but the vinyl has more inherent strength and maintains its shape better because of its higher modulus. Both have low-water retention and, although the Urethane appears more compatible to fluids such as kerosene and motor oil, the non-tacky nature of the vinyl makes it more compatible for use in saturation diving operations because no material growth will be experienced when the swimsuit is decompressed. If suits can be placed in a vacuum chamber after

a saturation dive, any growth of the Urethane can be eliminated with no permanent damage to the material. For surface diving this growth characteristic does not occur for any of the materials.

When the data for these materials are compared with those for Neoprene foam, it becomes obvious that the poor thermal conductivity, compressibility, and water retention properties of the standard Neoprene foam at the 1000 FSW depths negate consideration of this material for deep-dive applications.

#### CONCLUSIONS AND RECOMMENDATIONS

Data and theoretical considerations indicate that thermal-conductivity values have not been optimized, but since considerable efforts made to approach optimum values have failed, it seems this goal is not easily achievable. It may be that any further effort in this regard would result in little success.

As was shown previously, the gas entrapped in the glass spheres has a conductivity equivalent to normal room air even though the spheres have a partial vacuum internally which is created when they are formed. If these particles could be formed in a high-vacuum oven rather than in air, lower thermal conductivity would be achieved. These new spheres would simply replace the current one used in the Urethane or PVC composite. As a result, the new swimsuit would be theoretically about 15% less conductive than a suit made from the Urethane and PVC composites described previously.

Improvements in properties such as weight would be nominal because of the loading restriction to achieve suitable drapeability. The need to have highly plasticized materials to obtain good drape substantially precludes the possibility of having a non-flammable material even in normal atmospheres. Therefore, it would be highly doubtful that non-flammability could be achieved for diving-chamber atmospheres.

It is therefore felt that, at best, further development efforts using a syntactic-foam material approach would produce a material having characteristics only nominally better than those discussed. It would be more beneficial to apply future efforts to the special suit design and fabrication problems that these materials require. For instance, since these syntactic foams do not have the form-fitting (stretch-flex) properties of Neoprene foam which permits the material to follow body movements, the utilization of standard, wet-suit, fabrication techniques would cause a substantial amount of water movement into and out of the suit while the wearer is swimming so that material insulation would be completely compromised. It is therefore felt that future efforts should be targeted to creating the special suit designs these materials will require to be effective.

The Unit-developed, polyurethane-hollow-glass-microsphere, composite material and a proprietary, industrially-developed, polyvinylchloride-hollow-glass-microsphere, composite material showed performance parameters desirable for deep-sea swimsuits. Both have good drape characteristics at normal ambient temperatures as well as temperatures down to 20°F. The PVC maintains good drape even at 0°F. They both compress less than 3% at depths down to 1000 FSW and, as a result, they maintain much of their initial

insulative qualities regardless of depth (maximum change less than 13%). These materials provide greater insulation for equivalent thicknesses of the currently used Neoprene foam at a depth greater than 20 feet, although at essentially atmospheric pressure, they are significantly poorer than the foamed Neoprene. These materials are also substantially heavier than the Neoprene foam and did not achieve thermal-conductivity values as low as thought possible. Thermal-conductance tests on wet-style swimsuits fabricated from the PVC and Urethane materials substantially confirmed similar data obtained on material samples with a guarded-hot-plate device.

Finally, the Urethane and vinyl materials can be considered as suitable substitutes for each other for a deep-dive swimsuit application.

## APPENDIX A. TEST METHODS

### Thermal Conductivity

Cenco Fitch Method - Thermal conductivity is determined by use of this transient, one-dimensional, heat-transfer technique. Thermal diffusivity is determined from which thermal conductivity can be computed. The detailed procedure for this method is given in ASTM test method D2214. This method could only be used for evaluations at normal atmospheric conditions.

Guarded-Hot-Plate Method - The device used for these studies was specially designed so that thermal conductivity could be determined under simulated water depths. Details of the device are given in reference 4. Unlike the Cenco Fitch Method, this method determines thermal conductivity under steady-state, heat-transfer conditions. The device is similar in character and function to that described in ASTM test method C-177.

### Thickness Change Test

A device to determine thickness change under simulated deep-sea depths had to be designed for this purpose. Details of the device are given in reference 4. The device can measure thickness changes as small as 0.002 inch at any depth condition desired.

### Material Density

This property was computed after a material sample of known volume was weighed.

### Burst Strength

The material samples were subjected to hydrostatic pressure while held in a ring-type clamping device. The pressure at which water penetration occurred was assumed to be the bursting strength of the material. This test method is detailed in FED-STD-191 TM 5512.

### Abrasion Resistance

For this test the samples were subjected to multidirectional rubbing with Jewelite #2204 waterproof paper as the abradant. The abrasive head was weighted with a 1-pound weight and the material held in a ring-type specimen holder was inflated by pressurizing the sample to 2.5 psi. The criterion for stopping the test was the breakthrough of the backing fabric on the samples. More details of the test method are given in FED-STD-191 TM 5302.

### Chemical Resistance

The method of test was ASTM TM D543. Material effects were judged by weight and size changes as well as by visual observations.

## Drape Stiffness

The method used for determining this property was similar to FED-STD-191 TM 5206 except that results were expressed as a modulus of flexure. The normal reporting procedure with this device did not include material thickness (this method is normally used for fabric tests in which thickness variations are not appreciable). Since sample materials in this study had widely varying thicknesses and densities, another reporting method had to be used. The flexure formula for a rigidly held cantilever beam with uniform loading was applied since the method of test is analagous to this condition. This formula would permit consideration of test material thickness.

$$E = \frac{WL^4}{8Iy} \quad \underline{1}$$

E = flexure modulus (psi)

W = distributed weight in lbs per inch of beam (sample) length

L = free length of sample (in)

y = sample end deflection (in)

I = moment of inertia for the specimen (in<sup>4</sup>)

$$\text{where } I = \frac{bh^3}{12}$$

b = width of material (in)

h = thickness of material in inches

This formula was rewritten into a more useful form as:

$$E = \frac{3}{2} \frac{pL^4}{yh^2} \quad \underline{2}$$

where p is the material density (#/in<sup>3</sup>). For the test device y is always equal to y = L tan 41.5° = .885 L substituting in 2.

$$E = 1.7 \frac{pL^3}{h^2}$$

## Water Retention

Samples were placed in a water bath, which was pressurized to 1000 FSW, and were allowed to remain at this pressure for 24 hours. Sample weight measurements were taken prior to and after the samples were removed from the pressurized water bath. Water retention was reported as a percent change in weight.

### Flammability

Flammability characteristics were determined in accordance with ASTM test method D1692.

### Oven Aging

The effect of temperature on weight loss was determined by placing material samples in a hot circulatory air oven for two weeks after which sample weight changes were ascertained. Oven temperatures of 110, 140, and 175°F were used.

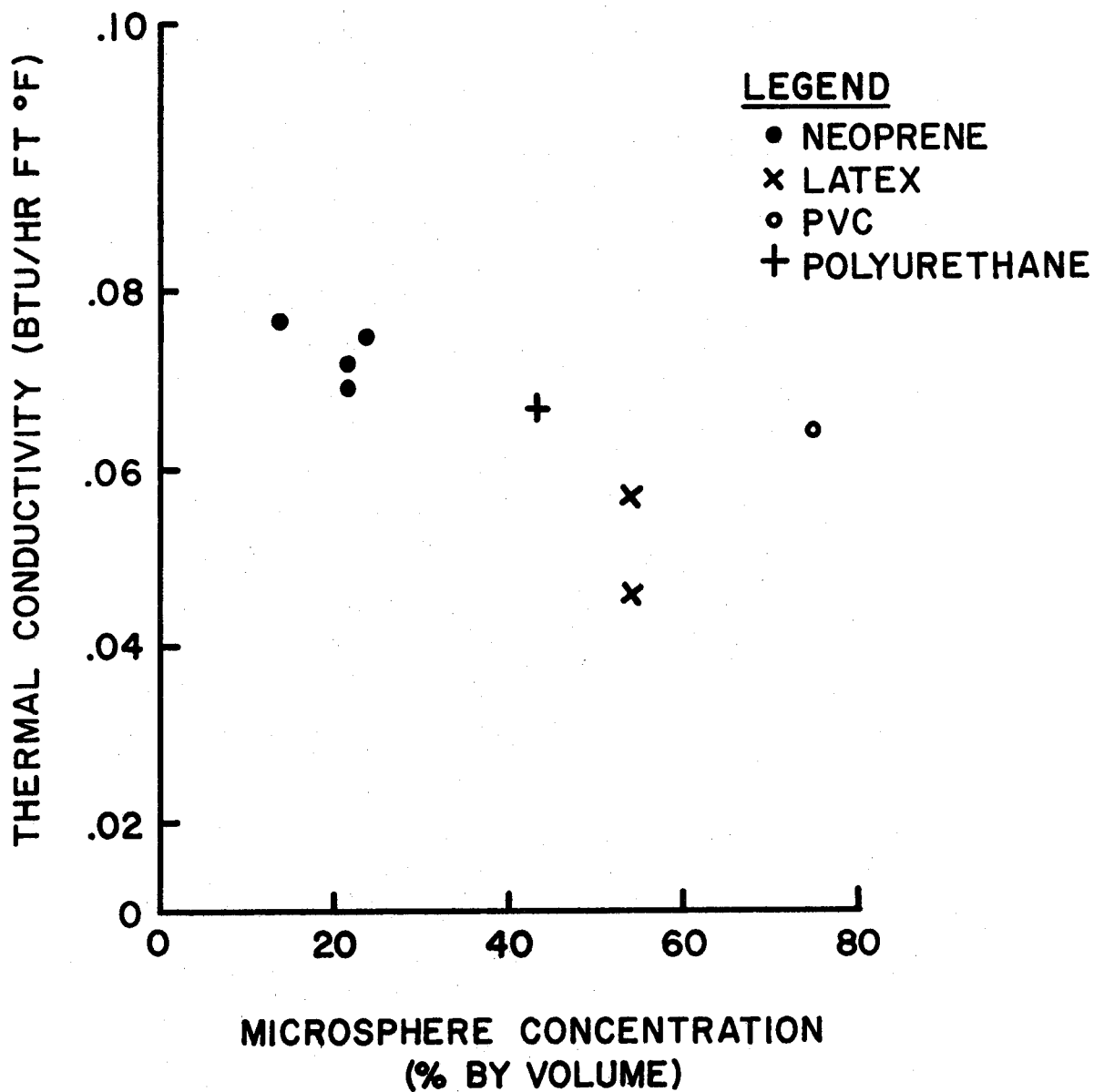
### Tensile-Elongation Tests

These tests closely paralleled method ASTM D638. Information was obtained on an Instron tester. A dumbbell-shaped specimen with an overall length of 3 inches and a test width of 1/4 inch was used. The gage length was 2 inches. Tester crosshead speed was 12 inches/minute.

### Stretch-Flex Test

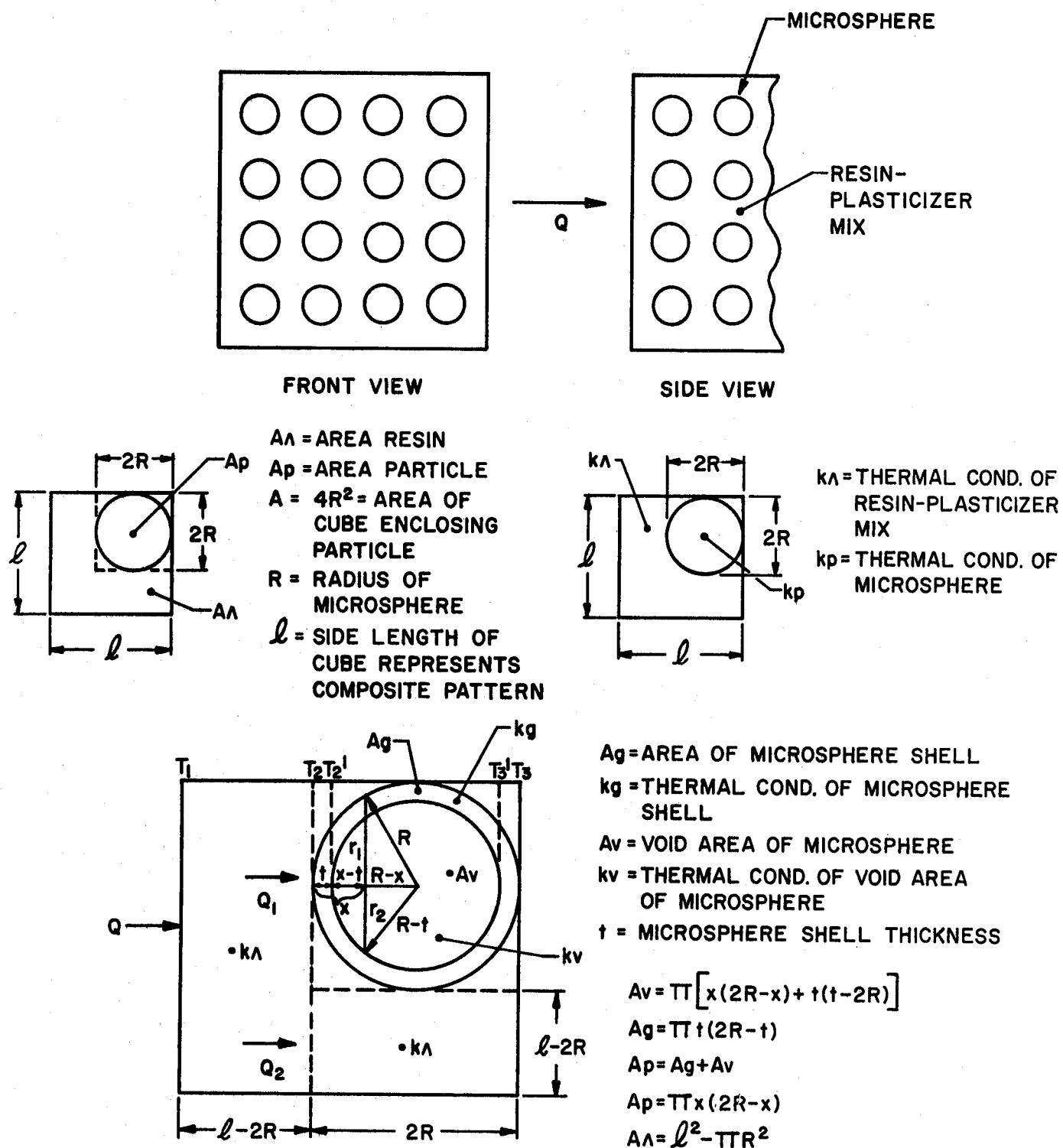
The device used to measure stretch-flex was specially designed for this study. The data from the device estimate the effort required to simultaneously stretch and flex the test materials under a biaxial stress condition. Details of the device and the test procedure for its use are given in reference 4.

## APPENDIX B. ILLUSTRATIONS



**FIG. 1 EFFECT OF GLASS-MICROSPHERE CON-  
CENTRATION ON COMPOSITE THERMAL  
CONDUCTIVITY FOR SEVERAL SUBMITTED  
SYNTACTIC-FOAM SPECIMENS**





**FIG. 2 MATERIAL-COMPOSITE THERMAL MODEL**

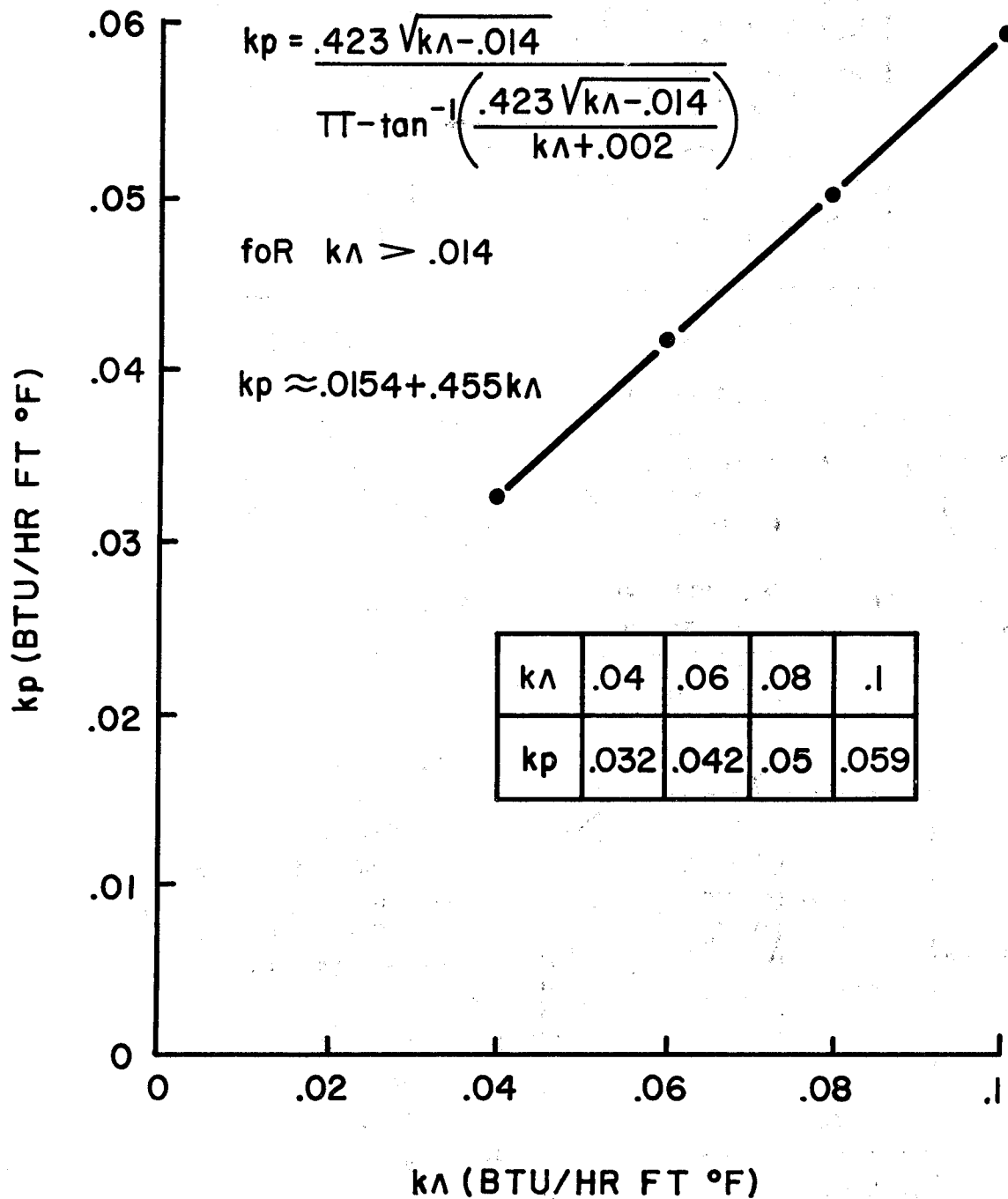
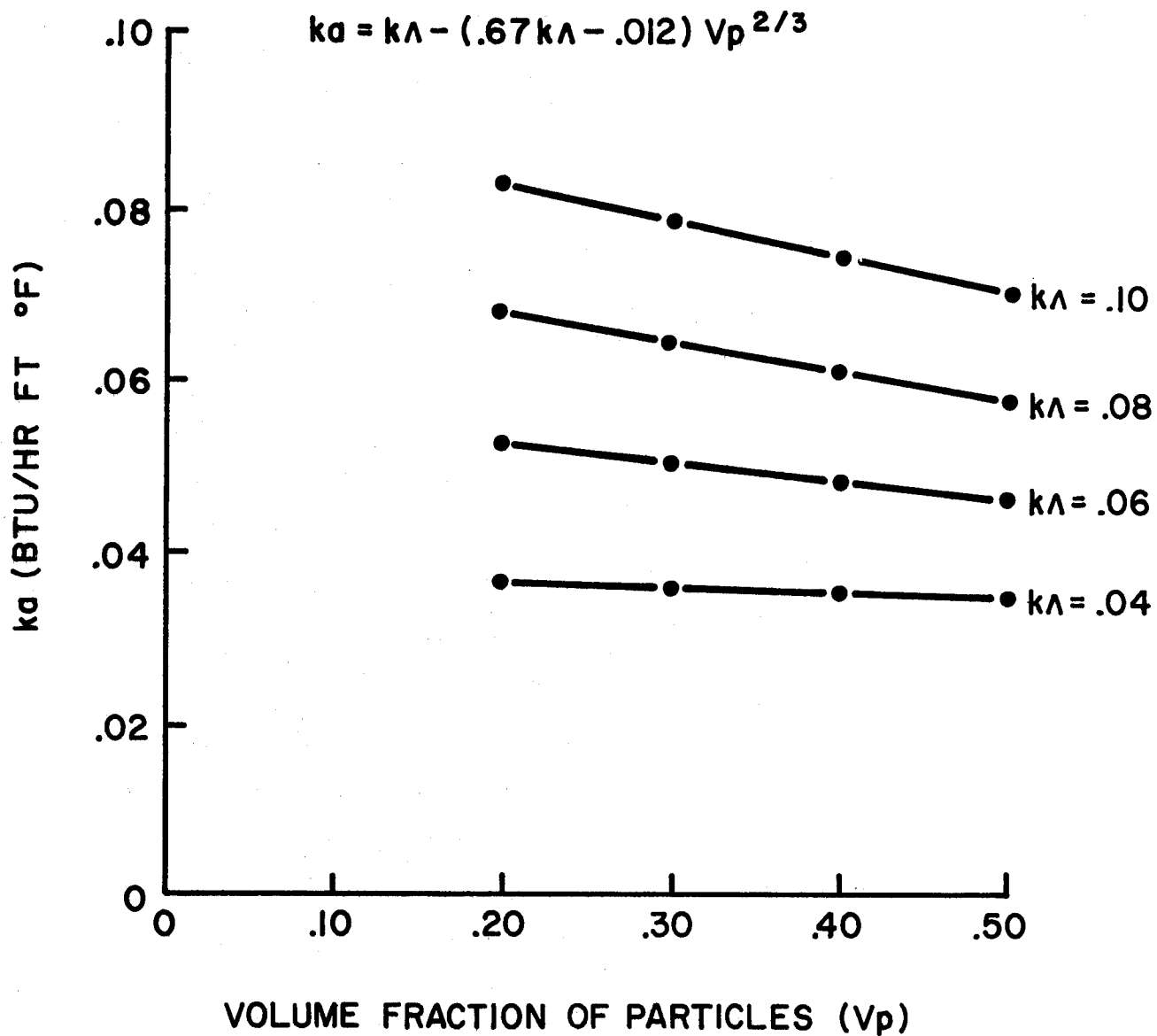


FIG. 3 EFFECT OF  $k\lambda$  ON  $k_p$



**FIG. 4 EFFECT OF CHANGES IN  
 $V_p$  AND  $k\lambda$  ON  $ka$**

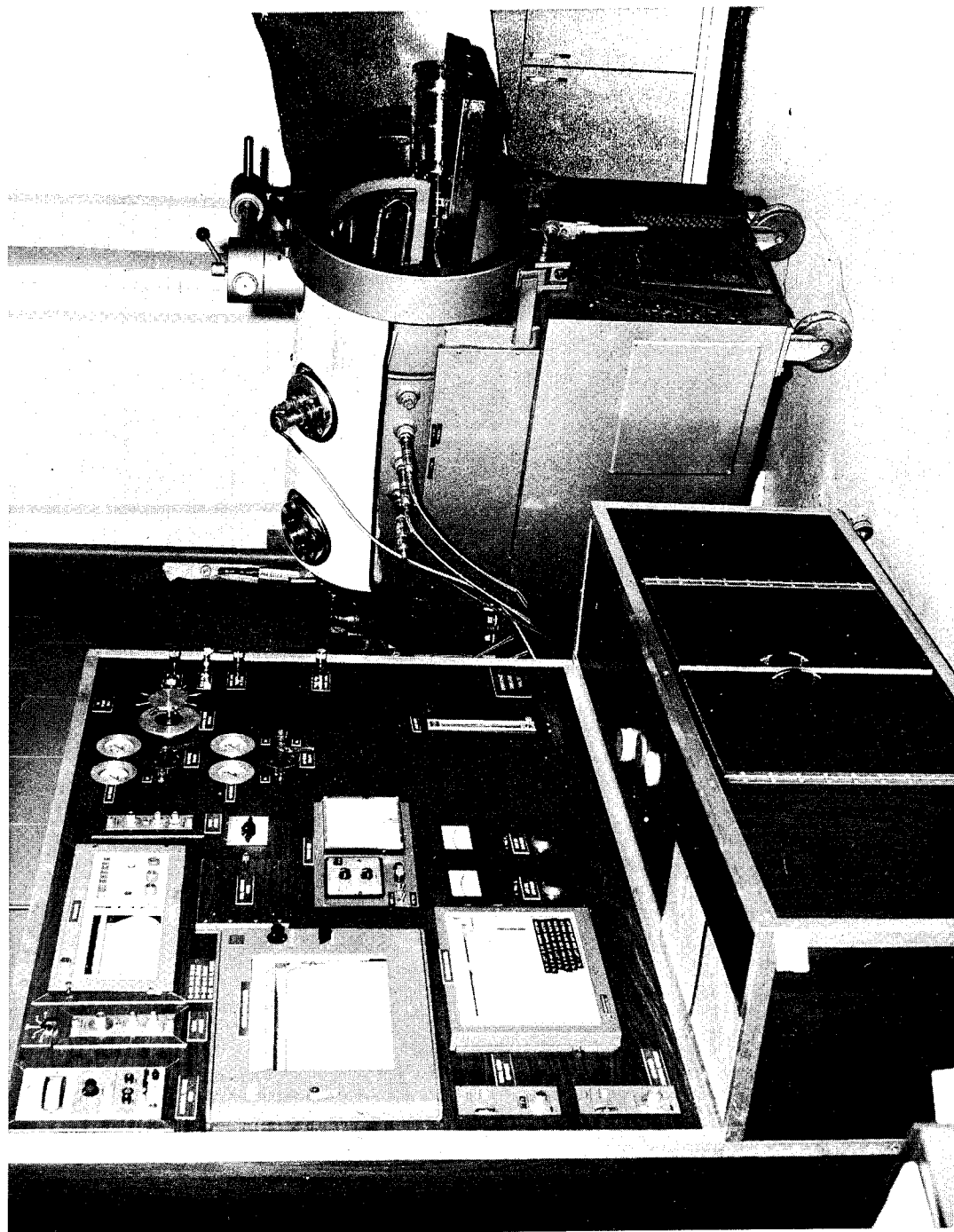


Figure 5 Hydrospace Simulator Facility containing the Instrument and Gas Control Equipment Console and the Pressure Chamber with the Thickness Tester.

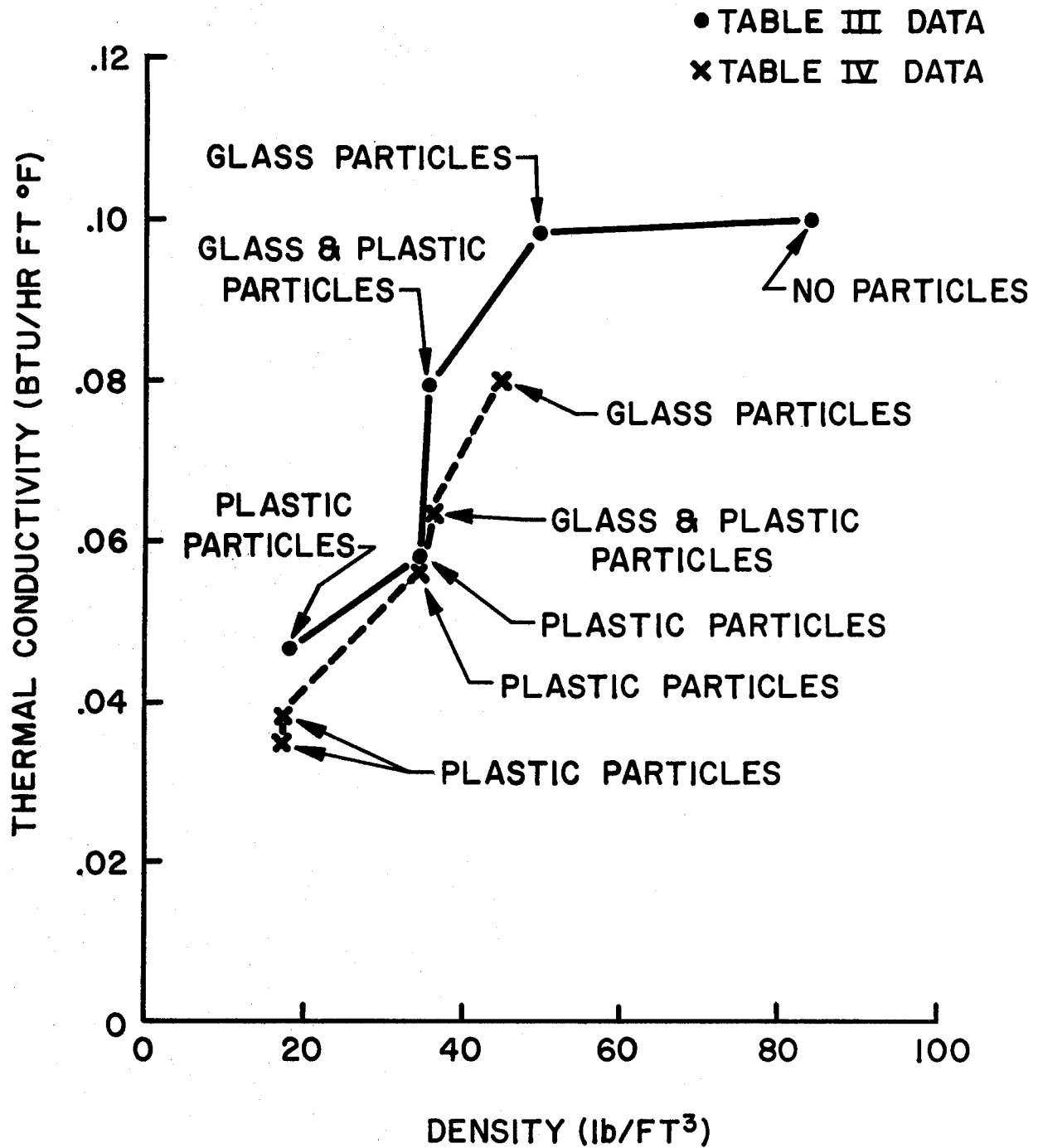


FIG. 6 EFFECT OF DENSITY AND PARTICLE TYPE ON THERMAL CONDUCTIVITY FOR TWO SIMILAR SAMPLE GROUPINGS

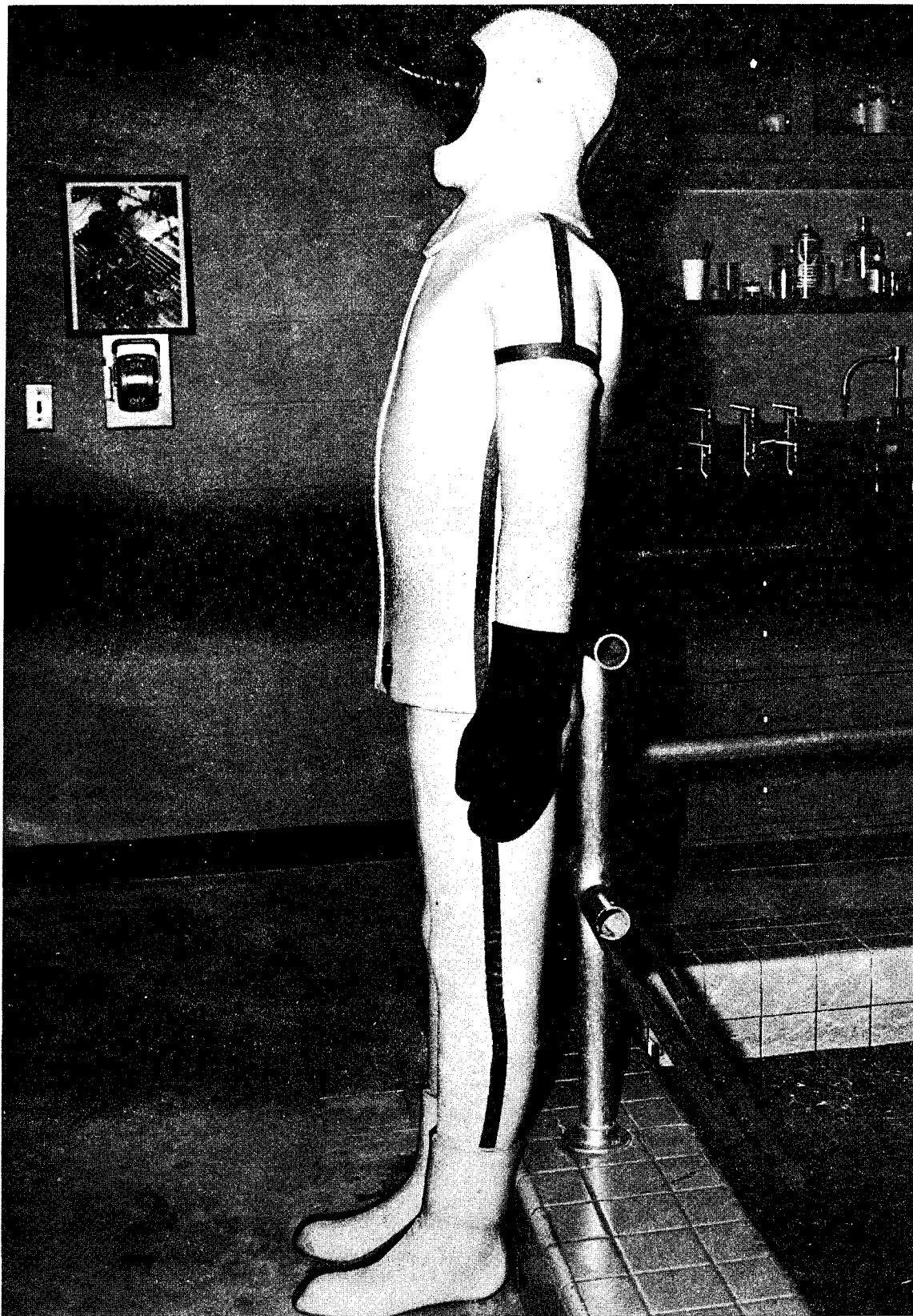


Figure 7 Wet Suit Fabricated from Polyurethane Composite Material and Mounted on Heated Copper Manikin



Figure 8 Wet Suit Fabricated from PVC Composite Material and Mounted on Heated Copper Manikin

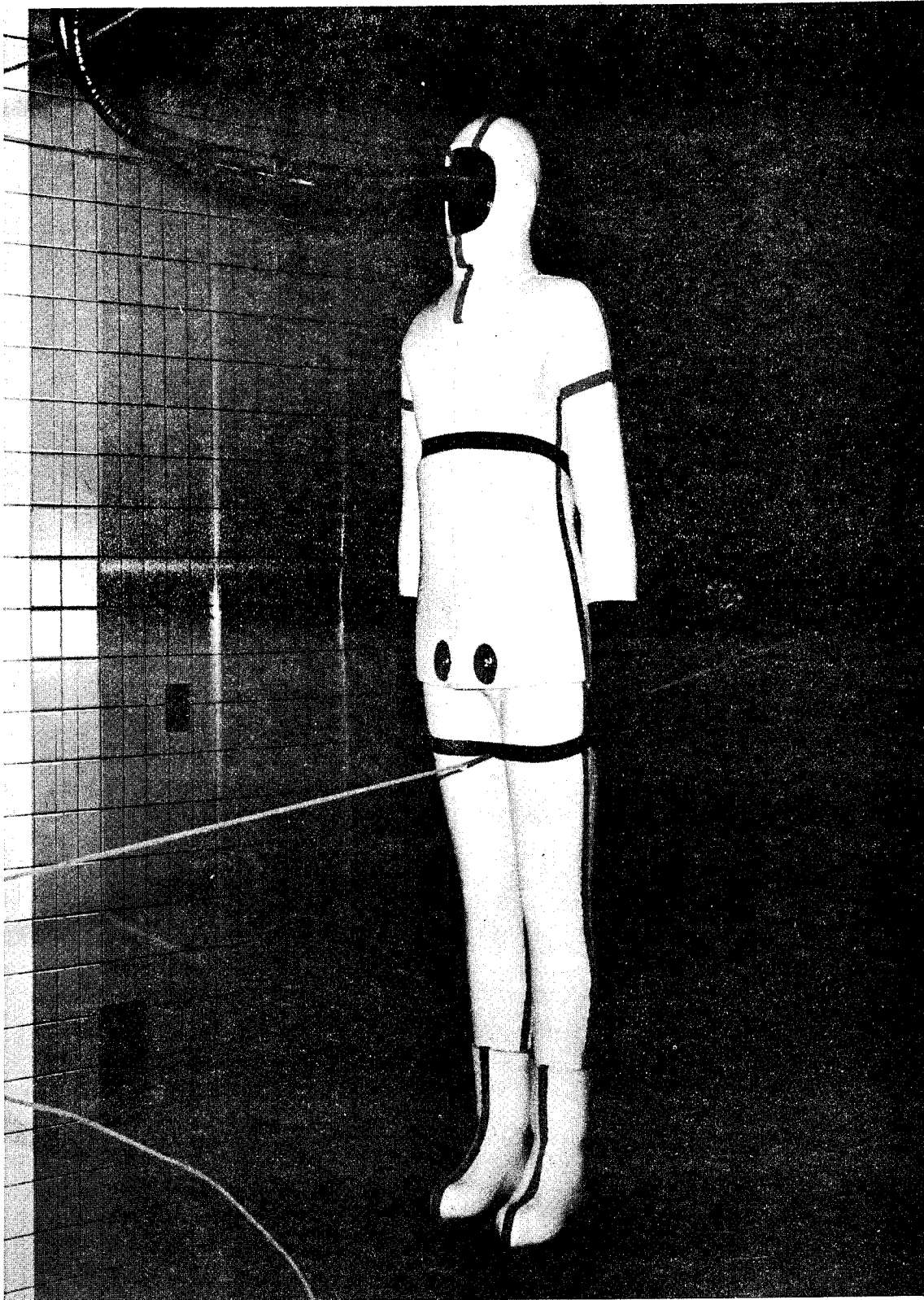


Figure 9 Polyurethane Suit as Tested in Pool Facility; Manikin is Approximately 1 foot Below Water Level





Figure 10 PVC Suit as Tested in Pool Facility; Manikin is Approximately 1 foot Below Water Level

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13. ABSTRACT <p>The Navy Clothing and Textile Research Unit (NCTRU) has developed a swimsuit material that meets the requirements of Navy personnel who operate at great sea depths for long periods of time. Two chemically distinct, flexible, syntactic foams--a Unit-developed, polyurethane, hollow-glass-microsphere composite and a proprietary, polyvinylchloride, hollow-glass-microsphere composite--have been produced which may prove useful for swimsuit applications in deep-sea environments down to 1000 FSW. (U)</p> <p>Tests showed that both materials were essentially incompressible to depths of 1000 FSW (less than 3%) and provided more insulation than currently used Neoprene-foam materials at depths greater than 20 FSW. The materials, however, were considerably heavier than the foam although significantly less dense than sea water. (U)</p> <p>Standard wet-style swimsuits were fabricated from these experimental materials for verification of sample thermal-conductivity data. Suit conductivity tests performed on an instrumented copper manikin substantially confirmed the material test data obtained with a guarded hot-plate device. During construction of the suits it also became apparent that special designs and fabrication techniques would have to be developed to utilize these materials most effectively. (U)</p> <p>(see other side)</p>			

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	ROLE	WT	ROLE	WT	ROLE	WT
Deep-Sea Swimsuit Materials Polyurethane Composite Material Polyvinylchloride Composite Material Wet-Style Swimsuits Thermal Conductivity						
13. ABSTRACT (continued)						
<p>The thermal-conductivity results measured for both material composites were higher than expected based upon theoretical derivations, indicating that further improvements may be possible in this property. The higher conductivity values may indicate that, when the material is compounded, some of the spheres may be fractured. As a result, solid-glass particles coexist with the hollow spheres, limiting to some degree the ability of the spheres to reduce conductivity to the expected level.(U)</p> <p>Since the many efforts to approach optimum values have failed, it seems this goal is not easily achievable. It is therefore felt that further development would produce a material only nominally better than the polyurethane and PVC composites. It is recommended that future efforts be expended on the special suit design and fabrication problems that these materials require to best use their particular characteristics.(U)</p>						

UNCLASSIFIED

Security Classification